

# Coupling between adsorbate vibrations and an electronic surface state

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The coupling between electrons and atomic and molecular vibrations at surfaces is of crucial importance for understanding energy transfer between adsorbate atoms and surfaces. In particular, nonadiabatic processes are important since these contribute to the dampening of adsorbate vibrations and are thus key to controlling surface reaction mechanisms. Despite this importance, quantitative, direct measurements of the two coupled components, the adsorbate vibrational mode and the underlying electronic continuum, with adequate resolution and sensitivity are rare<sup>1,2</sup>. Most of the work done so far has been on the phonon side of the problem,<sup>3</sup> with little attention to see the effects on the electronic states directly. Fundamental considerations of causality show that the electronic response should manifest as a change in the energy of the electronic states near the Fermi level, with an energy scale comparable to the phonon energies.<sup>4</sup>

With the advent of high resolution photoemission spectroscopy, there have been some recent studies of this electron-phonon coupling (EPC) effect on the detailed structure of the electronic bands for some special clean metal surfaces.<sup>5,6,7,8,9,10</sup> In this study, we apply similar techniques to study the EPC affect for electrons at the W(110) surface with the vibrations of adsorbed hydrogen atoms. Not only can we extract the EPC coupling parameter  $\lambda$  from the data, but we can also vary the EPC by substituting deuterium for hydrogen. The observed isotope effect confirms the role of phonons in the effects observed on the surface states.

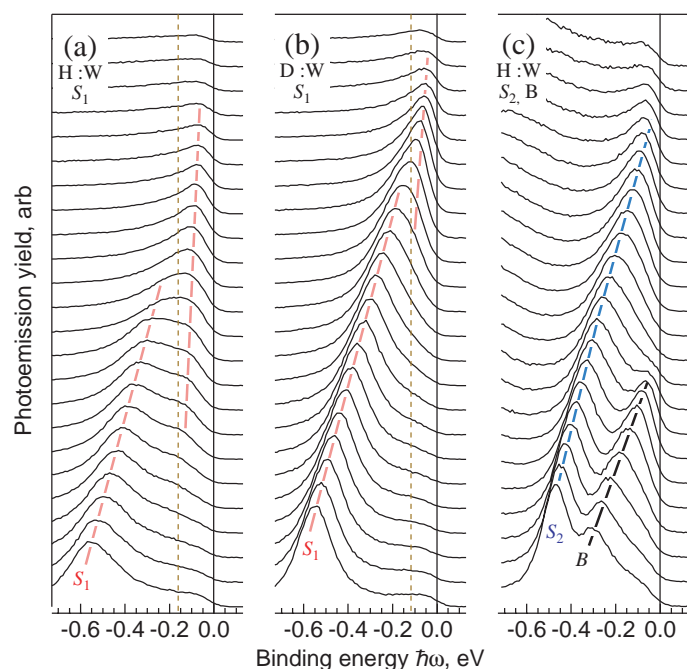


Figure 1. Bottom to top, a series of photoemission spectra for increasing  $k$  for various electronic bands of W(110). (a) the band crossing of surface state  $S_1$  in the presence of H. (b) the same band  $S_1$  in the presence of D. (c) the crossing of surface state  $S_2$  and bulk state B in the presence of H.

Figure 1 shows the main result.

In the left panel, we show a series of valence band spectra for a W(110) surface state  $S_1$  as it crosses the Fermi level. Each spectrum is obtained for electrons at various angles  $\theta$  and hence momenta  $k$ . Rather than simply crossing the Fermi level, this state is observed to lose intensity while a second state arises near the dashed line just below  $E_F$ . This second state takes over the overall intensity as it crosses  $E_F$ . The vertical dashed line is actually the energy of the symmetric stretch vibrational mode, determined independently by phonon scattering measurements<sup>11</sup>. The interpretation for the splitting into two states is that above and below the phonon energy  $\hbar\omega_0$ , the hole created during photoemission has two characters: below  $\hbar\omega_0$ , it decays by emission into phonons, thus increasing its width due to finite

occur because the hole has insufficient energy to create real phonons; nevertheless the hole carries a cloud of virtual phonon excitations which raises the effective mass of the hole. This causes the slope of the dispersing band to change, which is evidenced by the red lines in fig. 1(a). Fig. 1(b) shows what happens when deuterium is substituted for hydrogen. The principal effect should be that since D weighs twice as much as H, the vibrational frequency and hence energy scale is reduced by  $\sim\sqrt{2}$ . Therefore the same effects (band splitting, change in slope between the dashed line and  $E_F$ ) on the band in fig. 1(a) are seen in fig. 1(b), except the energy scale is compressed towards  $E_F$  by  $\sqrt{2}$ . As a control, we also measured a different surface state ( $S_2$  in fig 1(c)) which is characterized by a much smaller spatial overlap to the surface region because of its proximity to the bulk band edge ( $B$  in fig. 1(c)). Neither the bulk state  $B$  nor this second surface state  $S_2$  shows the splitting or slope change near  $E_F$  as expected. Nor were any of these effects observed for the bands on the clean surface.

The main implications of our research are the following: first that we can see that not only is energy transferred from the vibrational to the electronic manifolds, but also the opposite happens. The characteristic time, proportional to the inverse linewidth of the hole, is a few femtoseconds, which is certainly very fast for a typical step in a thermal chemical reaction. The second point that the electron phonon coupling can be tailored at interfaces by adding adsorbate atoms. The effects we see were much stronger for the adsorbate-covered surface than for the clean surface, even though the same electronic surface states are present for all coverages of hydrogen.

This work has been accepted for publication where further details are provided.<sup>12</sup>

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